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Dissolved rare earth elements in the Black Sea

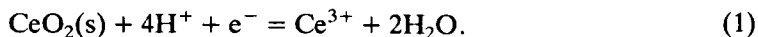
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Abstract—Concentrations of rare earths in the deep anoxic Black Sea are about one order of magnitude higher than in normal open ocean waters. From a minimum at the suboxic–anoxic interface at about 107 m depth, concentrations increase strongly to a maximum at about 300–400 m depth. Concentrations of Ce range from 3 pM at 107 m to 205 pM at 300 m depth, partly as a result of its oxidation–reduction chemistry. The other, strictly trivalent, rare earths exhibit similar trends albeit not as dramatic as for Ce. Minima and maxima are dominating features throughout the rare earth elements (REE) series, yet with increasing atomic number the gradients become more subtle. No distinct trends are observed for the REE at the primary maximum of particulate Mn at $\sigma_\theta = 15.65$ (~75 m depth) in the intermediate suboxic zone. The dissolved REE minima at 107 m exist at ambient sulfide levels of about 1 μM and coincide with a strong particle maximum. At the very same $\sigma_\theta = 16.10$ density horizon a distinct maximum of phototrophic bacteria (with concomitant levels of chlorophyll *a*) has been reported as well as the secondary particulate Mn maximum. From thermodynamic considerations the latter was not expected to occur within sulfidic waters. Apparently all REE are involved in the redox-cycling across the suboxic–anoxic interface, where the abundant bacterial particles most likely serve as carriers, possibly through Mn-oxide surface coatings. While Ce exhibits active oxidation–reduction chemistry, there is little or no evidence suggesting the reduction of dissolved Eu(III) to Eu(II).

INTRODUCTION

THE rare earth elements (REE) or *lanthanides* comprise an extremely coherent group of transition elements. Their common valency is the (III) oxidation state. In seawater they only exist in the dissolved trivalent form, mostly complexed though as carbonate species (BYRNE *et al.*, 1988). However, in the oceans dissolved Ce(III) can also be oxidized to an insoluble Ce(IV) state, presumably CeO_2 . This leads to the well-documented depletion of Ce relative to the other REE in the open oceans (DE BAAR *et al.*, 1983, 1985a,b). Under reducing marine conditions the reaction takes place in the reverse direction:



The dissolution of solid Ce(IV) phases then yields enhanced concentrations of dissolved

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Ce(III) as has been reported in several marine environments (DE BAAR *et al.*, 1983, 1985, 1988; ELDERFIELD and SHOLKOVITZ 1987; SHOLKOVITZ *et al.*, 1989; GERMAN and ELDERFIELD, 1989, 1990). The positive and negative Ce anomalies resulting from this reaction have almost exclusively been observed within the oceanic realm. Continental rocks and streams do not show Ce anomalies, i.e. the Ce(IV) state appears unique to the marine environment.

Eu is the only other REE exhibiting multiple oxidation states in natural environments. Rather than becoming oxidized it can be reduced from the common Eu(III) to the more exceptional Eu(II). Fractionation of Eu(II) is frequently observed in mantle-derived magmatic rocks, yet is implausible in low temperature marine geochemistry.

Recently the seawater concentration of Ce, the light REE (La, Nd, Sm, Eu) and to a lesser extent the heavy REE was generally found to be elevated in the anoxic Cariaco Trench (DE BAAR *et al.*, 1988). In the Cariaco Trench the transition from oxic to anoxic is very abrupt and intermediates (nitrate reduction, Mn reduction) in the well-known general reduction sequence cannot be resolved. From thermodynamic considerations the dissolved Ce(III) was reported to be undersaturated in the anoxic waters, but oversaturated in the overlying oxic waters. The other, strictly trivalent, REE appeared to be carried along with the reduction–oxidation cycle of solid/dissolved Mn. Vertical gradients at the oxic–anoxic interface were interpreted as to rank the rates of “redox-cycling” in the order (i) Mn, (ii) Ce and (iii) other REE.

In the hypersaline, anoxic Bannock Basin (East Mediterranean) very strong REE enrichments were found at the oxic–anoxic interface as well as in below two brine layers (SCHIJF *et al.*, 1989a). A similar but more modest REE enrichment was also found in suboxic waters of the equatorial Pacific Ocean (DE BAAR *et al.*, 1985a), the northwest Indian Ocean (GERMAN and ELDERFIELD, 1990), the oxygen-deprived bottom waters of Chesapeake Bay (SHOLKOVITZ and ELDERFIELD, 1988) and the seasonally anoxic Saanich Inlet (GERMAN and ELDERFIELD, 1989). These water column observations suggest active mobilization of REE during early diagenesis. High REE concentrations were indeed found in pore waters of nearshore Buzzards Bay sediments (ELDERFIELD and SHOLKOVITZ, 1987; SHOLKOVITZ *et al.*, 1989).

Early studies of artificial radionuclides of the REE (mostly ^{141}Ce , ^{144}Ce and ^{147}Pm) from bomb fallout have not dealt with reducing marine environments (review in DE BAAR, 1983). The ^{144}Ce released from nuclear fuel reprocessing plants is apparently strongly retained by the finest size fraction of marine sediments (HETHERINGTON and JEFFERIES, 1974; GUEGUENIAT *et al.*, 1979). The latter appears in contrast with the now emerging viewpoint of rapid (reductive) mobilization of natural (stable) Ce under reducing conditions (this and aforementioned papers). The fate of REE radioisotopes arising from Chernobyl fallout in both oxygenated waters (FOWLER *et al.*, 1987) as well as the anoxic Black Sea (BUESSELER *et al.*, 1987; BUESSELER *et al.*, 1990) has important implications for our study, and vice versa.

Finally the reduction of Eu(III) to Eu(II) thus far has never been reported in low temperature waters. On the other hand it commonly produces elevated Eu concentrations in high temperature, reducing, hydrothermal vent fluids (MICHARD *et al.*, 1983; MICHARD and ALBAREDE, 1986; MICHARD, 1989; ELDERFIELD and SHOLKOVITZ, 1987 as cited by ELDERFIELD, 1988).

Here we report on the dissolved REE distributions in the Black Sea. Preliminary results of this study have been summarized previously (SCHIJF *et al.*, 1989b, 1990). Early estimates

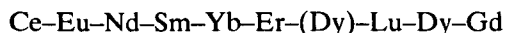
of REE in the Black Sea (KOLESOV *et al.*, 1975) and in single samples from deep trenches (Cariaco Trench, Puerto Rican Trench, Costa Rica Dome, HØGDAHL, 1967) appear to be mostly of historical interest as they deviate considerably from our findings.

METHODS

The major station (BSK 2), occupied during R.V. *Knorr* cruise 134/12 (Black Sea Leg V) in July 1988, was in the center (43°N, 34°E) of the Black Sea Basin. Seawater samples were collected in pre-cleaned, Teflon-coated, 30-l samplers of the rotating ball-valve design modified after the "Go-Flo" type. Clean techniques were used throughout the sampling and analytical procedures. Upon recovery a nitrogen gas line was connected to the top of the samplers. An all-polyethylene filtration sandwich was connected at the bottom, holding 142 mm diameter, 0.2 μm pore size Nuclepore membrane filters. By application of 1 atm overpressure nitrogen the complete contents of the samplers were passed over the filters while maintaining an oxygen-free atmosphere over the seawater to avoid oxidation. Pre-cleaned 5-l PE bottles were rinsed several times with the filtered seawater. Filtered seawater samples were then collected in these bottles and acidified to pH 2 with triple quartz distilled 6 N HCl. Filters were stored in the freezer for future analyses. During the preceding Leg III similar clean methods were used for the collection and processing of samples for the study of Mn, Fe and several other transition metals (LEWIS and LANDING, 1991).

Extraction and purification of the REE were carried out as described in detail elsewhere (DE BAAR *et al.*, 1988). The REE were first extracted and separated from the major alkaline (Na, K) and earth alkaline (Ca, Mg, Sr, Ba) metals in seawater with a Chelex-100 column (DE BAAR, 1983). Then a second AG50W-X8 cation exchange column was used to remove final traces of these major elements. Elution of this column yields a fraction containing only La (and some Ce) preceded by another fraction containing all other REE. The removal efficiency of Ba on the column was estimated to be better than 99.99% judging from experiments with radioisotopes of Ba, Ce, Gd and Yb (DE BAAR, unpublished results). It is important that no Ba is present in the La fraction to avoid interference of the major Ba isotope (^{138}Ba) with the minor La isotope (^{138}La). Any such interference would make the $^{138}\text{La}/^{139}\text{La}$ ratio appear too high, which would lead to an underestimation of the La concentration.

Isotope dilution mass spectrometry was performed with a Finnigan MAT 261 mass spectrometer with a 13 position magazine using stepwise heating for arrays consisting of two Re filaments. Samples were loaded on one Re filament, the opposite Re filament serving towards enhancing ionization. Isotopic ratios were determined in the single collector (peak jumping) mode. Initially the fractions containing all REE except La were run. The evaporation sequence



appears specific to the use of Re (rather than Ta) filaments and the source geometry of the Finnigan MAT 261 mass spectrometer and is different from the sequence reported for a VG mass spectrometer (THIRLWALL, 1982). The evaporation sequence for the Finnigan MAT 261 permits routine analysis of Lu rather than Dy and may lead to isobaric interference between Yb and Er isotopes. Analysis of Gd is hardly possible due to its poor ionization.

A magazine containing the La fractions was analysed separately. La was converted to La oxide by bleeding pure oxygen into the source at very low pressure during determination of the $^{138}\text{La}/^{139}\text{La}$ ratio. This serves towards suppressing isobaric interference by Ba, the latter presumably arising from spurious Ba emission from the Re filament. Ba ionizes less efficiently in the oxide form. Due to the very unstable Ba signal the isobaric interference by Ba cannot be adequately corrected for in the single collector (peak jumping) mode. Data were not collected until after the Ba oxide emission had decreased to undetectable levels, judging from the ^{137}Ba oxide signal. For about 50% of the samples that were analysed thus far, the persistent Ba background prevented reporting a final La value.

RESULTS

Vertical distributions of potential temperature and salinity yield a steady increase of density with depth (Fig. 1). The deep water in the Black Sea is more or less permanently stagnant, yet the resulting anoxic conditions are not at steady state but have now (1988) intensified (shoaled) as compared with earlier (1969) observations (MURRAY *et al.*, 1989). The most exciting feature is the existence of an intermediate suboxic layer where traces of dissolved O_2 are still present ($\text{O}_2 < 10\ \mu\text{M}$) without H_2S occurring ($\text{H}_2\text{S} < 1\ \mu\text{M}$; Fig. 2). In this zone one or two distinct nitrite maxima with different intensities and depth ranges

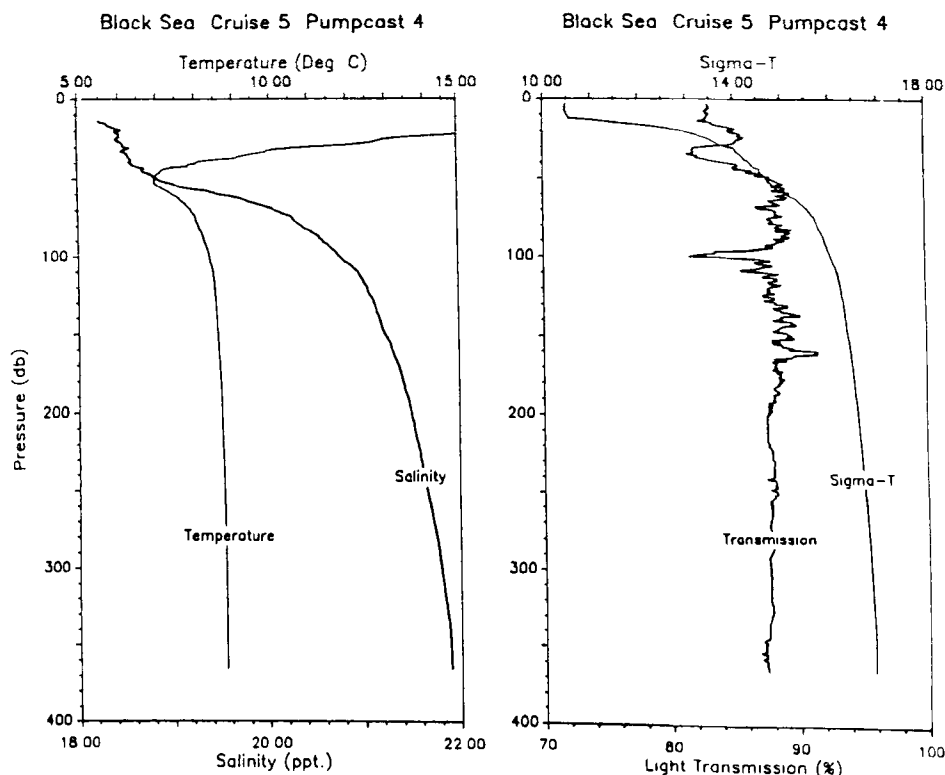


Fig. 1. Vertical profiles of potential temperature, salinity, density (σ_T) and light transmission (particulate matter) at Sta. BSK-2 in the Black Sea. Pumpcast 4 ($43^{\circ}03.32'\text{N}$, $34^{\circ}02.11'\text{E}$) of Leg V (25 July 1988), taken from CODISPOTI *et al.* (1989).

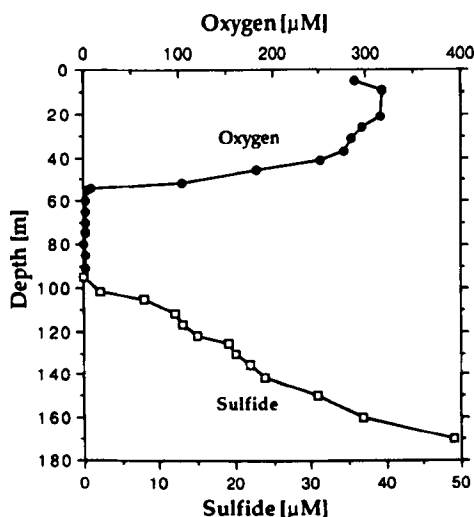


Fig. 2. Vertical profiles of dissolved O_2 and H_2S at Sta. BSK-2 ($43^\circ N$, $34^\circ E$), Leg III, Sta. 6 occupied 10–14 June 1988. Data from CODISPOTI *et al.* (1989).

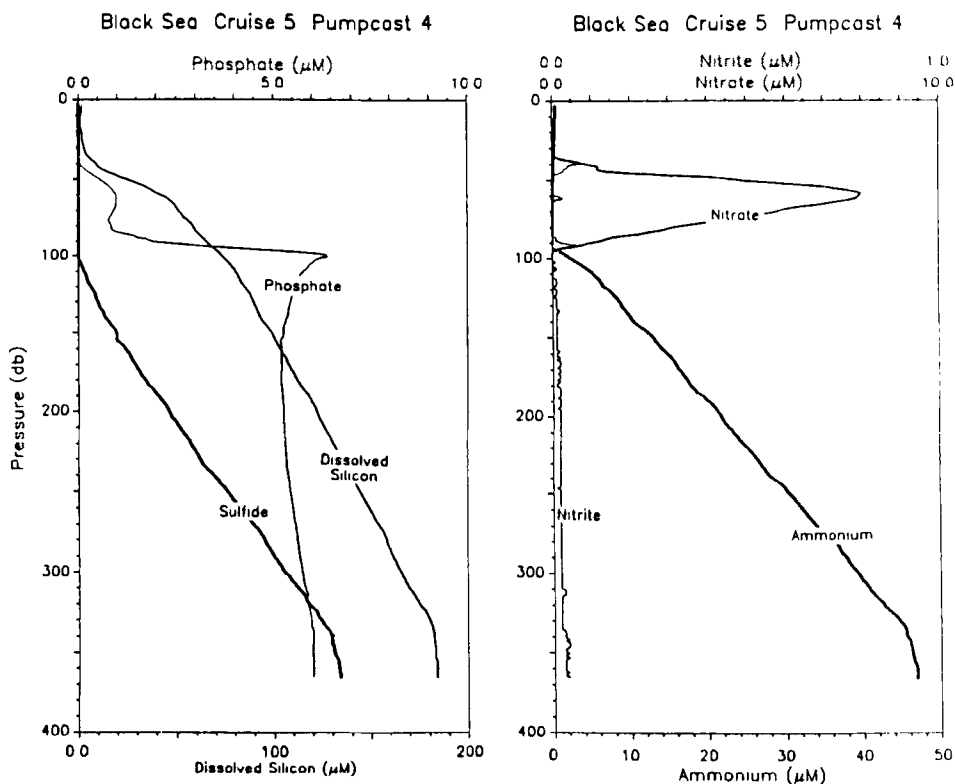


Fig. 3. Vertical profiles of dissolved silicate, phosphate, sulfide (a) and nitrogen species (b) at Sta. BSK-2 ($43^\circ 03.32' N$, $34^\circ 02.11' E$) in the Black Sea. Pumpcast 4 of Leg V (25 July 1988), taken from CODISPOTI *et al.* (1989).

were often found (Fig. 3). This and the ambient O_2 regime ($<10 \mu M$) indicate that nitrate reduction is taking place. The same suboxic zone is also the region where sharp gradients of dissolved as well as particulate Mn were found (Fig. 4). The dissolved Mn maximum of $8.6 \mu M$ resides near 180 m depth well within the anoxic waters. The primary maximum of particulate Mn resides within the suboxic zone at the $\sigma_\theta = 15.6$ density horizon (about 75 m depth) where oxygen concentrations are very low, ranging from 2 to $10 \mu M$ between various stations. This maximum, however, does not coincide with a particle maximum, judging from the overall particles (light transmission) profile (Figs 1, 4 and 7). This may suggest that particles at this specific depth are strongly coated with Mn oxides. On the other hand, one should bear in mind that there may be some temporal and spatial variability between Leg III when the samples for particulate Mn were collected and Leg V when the light transmission was recorded. The BSK-2 station is at a site where the two surface water gyres meet and the hydrographic features in the water column were observed to be quite variable within Leg V. The secondary particulate Mn maximum at the $\sigma_\theta = 16.1$ density horizon (about 105–115 m depth) is just within the anoxic water mass and quite unexpected from a thermodynamic perspective. This maximum of particulate Mn has been suggested to be an advective feature derived from margin sediments (TEBO, 1991) and coincides with a particle maximum (light transmission minimum) observed throughout the Black Sea in the April–July 1988 period of the five expeditions (Figs 1 and 7). The most intense expression of this particle maximum is found at the margins and at the central BSK-

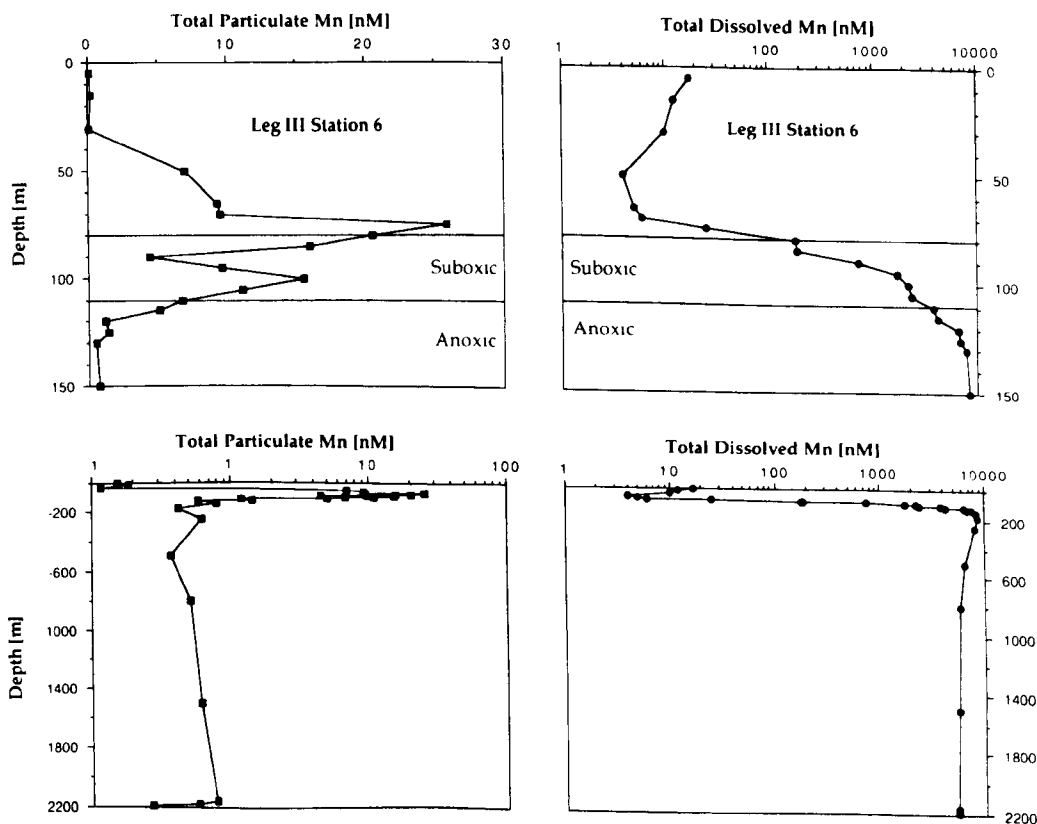


Fig. 4. Total particulate Mn and total dissolved Mn in the Black Sea, Leg III, Sta. 6 ($43^{\circ}04'N$, $34^{\circ}0'E$) occupied 10–14 June 1988. See also LEWIS and LANDING (1991).

2 site where the two gyres meet. Hence the very strong particle maximum at our station occupied in July may well originate from the margins. This very distinct particle layer has also been reported to be occupied by large numbers of obligate phototrophic, sulfide-oxidizing, bacteria (*Chlorobium*), as characterized by a great abundance of bacterial chlorophyll *e* (REPETA *et al.*, 1989). A distinct bacterial Chl *e* maximum was found during Leg II (May 1988) at the onset of detectable sulfide (75–85 m depth), within the very same $\sigma_\theta \approx 16.1$ density horizon where many other features are located (Fig. 7). Similar phototrophic bacteria (*Chlorobium*, *Chromatium*) have also been found at the shallow anoxic interface of Framvaren fjord (SØRENSEN, 1988). During Leg V we sampled these particles extensively; their contents (REE, Mn, Fe, pigments) have yet to be analysed.

At first glance the vertical distributions of the REE in the Black Sea (Fig. 5; Table 1) are strikingly similar to profiles reported for the Cariaco Trench (DE BAAR *et al.*, 1988). In both basins we find a distinct minimum for all REE at the onset of the anoxic deep water, coinciding with or slightly above the particle maximum. The dissolved minimum is most

Table 1. Concentrations (pmol kg⁻¹) of dissolved rare earth elements in filtered seawater collected at given depth (m) or pressure (dbar) at 43°N, 34°E in the Black Sea. The surface sample (0 m) is unfiltered. Omissions due to mass spectrometry problems (e.g. isobaric interference, unstable ion beam, filament breakage). Also listed are potential density σ_θ and (bottom row) the concentrations (μmol kg⁻¹) in shales for normalizing (Fig. 8)

Depth (m)	Pressure (dbar)	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu	σ_θ
0	0		30.77	23.19	5.52	1.45			13.2	9.7	1.48	10.52
30	30.5	33.1	16.53	21.82	4.76		7.4	10.0	9.2		1.28	14.2166
40	40.4		18.08	23.25	5.04	1.38			8.8		1.37	14.4307
40	40.4		18.66	23.64	5.03	1.36			9.0			14.4307
50	50.0		12.73	22.70	4.42	1.24			8.5	7.5	1.30	14.6184
60	59.5		5.36	16.94	3.56	1.04						15.3200
70	70.0	28.4	6.03	16.93	3.69					7.1		15.4830
85	83.2	19.4	3.54	12.24	2.58	0.76	4.2	6.4	6.6		1.11	15.7150
100	102.3		3.30	7.35	1.55	0.48			5.5	5.8	0.85	16.0180
107	106.9	16.8	3.95	7.23	1.44	0.45		4.2	5.3	5.5	0.95	16.0800
110	111.6	17.3	8.66	10.66	2.31	0.71		5.8	6.2	6.4	1.06	16.1033
115	115.9		19.20	15.68	3.29	0.96			8.1	8.3	1.21	16.1395
130	130.2		28.86	17.33	3.50		5.7	7.4			1.45	16.1700
160	159.5	56.4	109.41	44.98	9.16	2.56			12.7	12.2	1.67	16.4079
175	176.0		136.36	54.62	11.14	3.10					14.1	16.4901
200	200.5	64.5	153.75	63.10	12.73	3.51				14.8	1.70	16.5677
225	224.7		180.49	70.85	14.68	4.15				16.1		16.6534
250	251.0	90.3	196.72	77.45		4.16					2.06	16.7119
300	300.2		205	80.5								16.8265
400	401.2	89.7	198.17	80.66	16.04	4.50			16.8	17.6	1.99	16.9370
500	501.6	93.4	185.32	74.97	15.09	4.00			15.6	14.9	1.90	17.0264
700	701.1		159.15	67.49	13.70	3.75					14.5	17.1300
1050	1061.0		121.56	54.46	11.36	3.01					11.8	17.1968
1350	1365.1	68.8	114.33	51.73	10.24	2.84			12.0		1.46	17.2155
1600	1618.8		109.56	51.39	10.20	2.77			11.8	11.2	1.44	17.2209
1800	1822.1	69.0	100.13	48.42	9.86	2.69			11.1	10.9	1.41	17.2234
2172	2172	68.1	101.78	46.96	9.85	2.69			11.0	11.0	1.36	17.2230
Shales												
(μmol kg ⁻¹)		295	592	263	49.9	10.6	40.4	33.3	22.4	20.4	3.49	

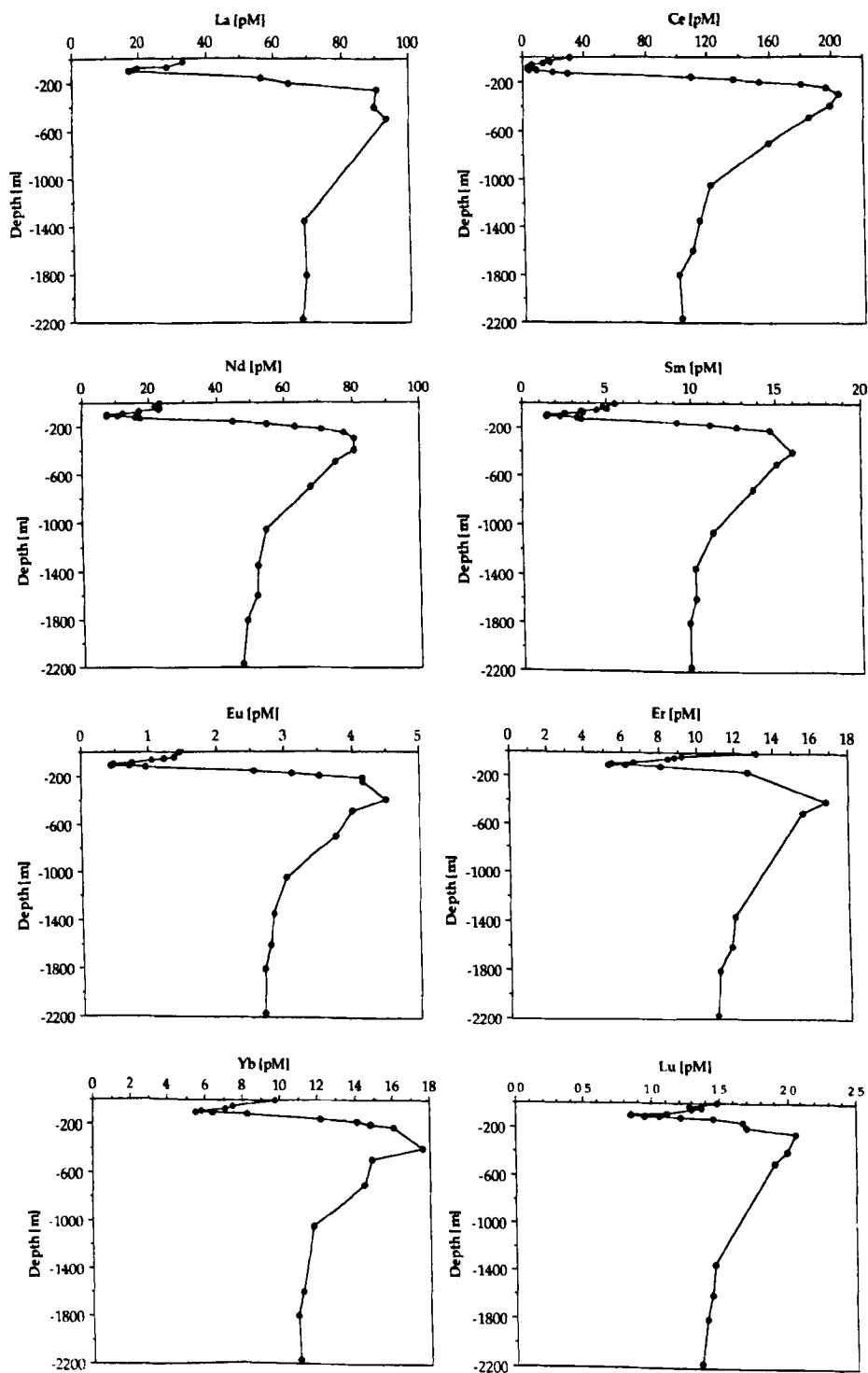


Fig. 5. Vertical profiles of dissolved rare earth elements (10^{-12} mol/kg seawater) in the Black Sea at Sta. BSK-2 (43°N, 34°E) occupied 15–26 July 1988 during Leg V.

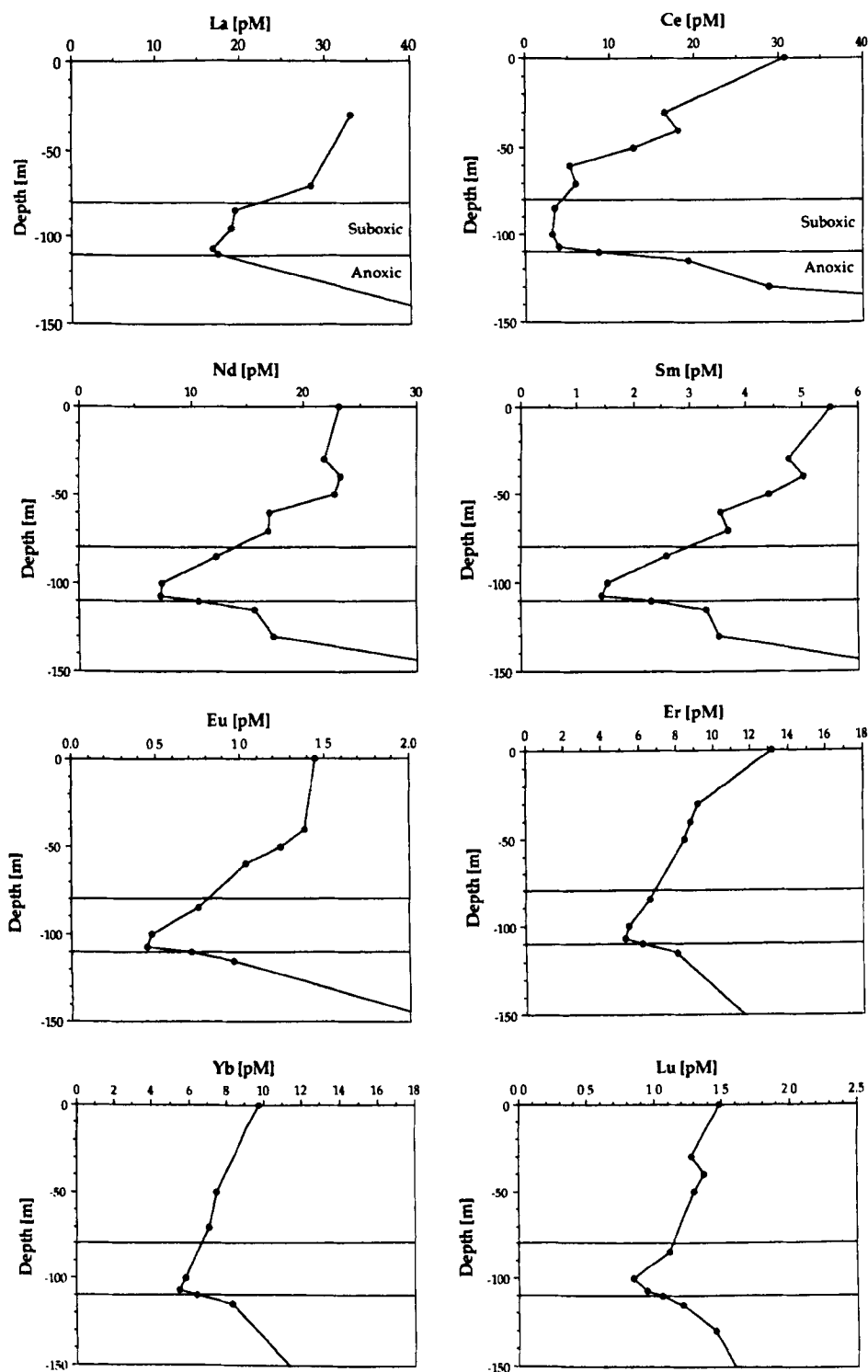


Fig. 6. Vertical profiles of dissolved rare earth elements (10^{-12} mol/kg seawater) in the upper 150 m of the Black Sea at Sta. BSK-2 (43°N, 34°E) occupied 15–26 July during Leg V. Note the distinct minima just above the suboxic–anoxic interface.

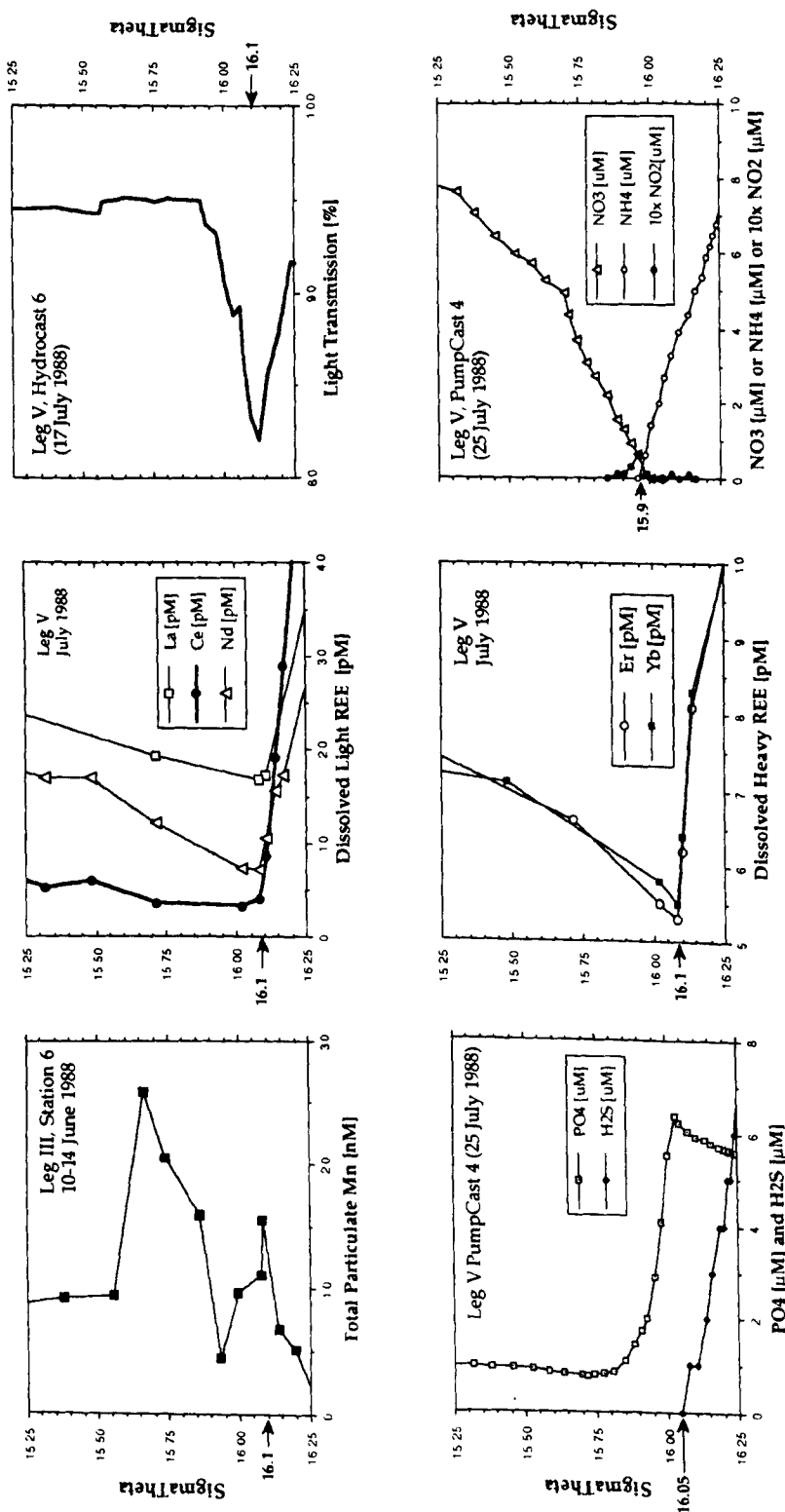


Fig. 7. Coincidence at the $\sigma_\theta = 16.1$ density horizon of the secondary particulate Mn peak (Leg III, Sta. 6 at 43°04'N, 34°0'E), the dissolved REE minima (Leg V), the particle maximum (Leg V) and the onset of the anoxic (sulfidic) waters (pumpcast 4 of Leg V at 25 July 1988). Not shown is the coinciding bacterial Chl *a* maximum (REPETA *et al.*, 1989). The corresponding depth varies considerably from hydrocast to hydrocast within the 75–110 m range. With respect to nitrogen (N) the transition from oxidized nitrate (NO_3^-) to reduced ammonia (NH_4^+) occurs at shallower density horizon $\sigma_\theta = 15.9$, also marked by a small nitrite (NO_2^-) peak. The dissolved phosphate (PO_4^{3-}) peak at $\sigma_\theta = 16.0$ is in itself intriguing but does not appear to be related to the REE geochemistry. Hydrographic data taken from WHITE *et al.* (1989), nutrients data taken from CONISOPH *et al.* (1989).

striking for the light REE, notably Nd, Sm and Eu. Curiously enough the distribution of Ce is quite constant across the Black Sea suboxic layer from about 80 to 105 m depth (Fig. 6). Recently reported REE profiles for the seasonally anoxic Saanich Inlet also exhibit distinct minima (GERMAN and ELDERFIELD, 1989). However, both in the Cariaco Trench as well as in Saanich Inlet the dissolved REE minima and particulate (Mn) maxima reside above the oxic–anoxic interface, at low but discernible ambient O_2 levels ($\sim 2 \mu M$ at 280 m in the Cariaco Trench; $\sim 50 \mu M$ at 140 m in Saanich Inlet) without any sulfide present.

In contrast the Black Sea exhibits minima of dissolved REE that coincide with strong particle maximum probably consisting of bacteria as well as Mn oxides, found at a depth where no more O_2 is present and typically at the first discernible ($\sim 1 \mu M$) sulfide (Fig. 2). The various depth profiles in Figs 1–6 represent different hydrocasts at Sta. BSK-2 from Legs III and V. There is some variability in the depth of the various chemical features, presumably due to the dynamics of two meeting gyres as well as the suggested interleaving of water layers (BUESSELER *et al.*, 1991). However, when plotted as profiles vs potential density the virtually perfect coincidence of the aforementioned extrema is obvious (Fig. 7). The transition from oxidized nitrate (NO_3^-) to reduced ammonia (NH_4^+) occurs at a shallower density horizon $\sigma_\theta = 15.9$ also marked by a small nitrite (NO_2^-) peak. The dissolved phosphate (PO_4^{3-}) peak at $\sigma_\theta = 16.0$ does not appear to be related to the REE geochemistry.

The actual maxima of dissolved Ce and other REE are found at 300 and 400 m depth, respectively (Fig. 5). The absolute REE concentrations are about four-fold those found in the Cariaco Trench, a distinct albeit not as dramatic difference as for dissolved Mn [~ 400 nM in the Cariaco Trench (JACOBS *et al.*, 1987) vs ~ 8600 nM in the Black Sea] or H_2S (~ 50 vs $\sim 350 \mu M$). Among the REE the overall gradient is generally strongest for Ce, then decreases with increasing atomic number from Nd to Lu (Fig. 5). This ranking was also observed in the Cariaco Trench (DE BAAR *et al.*, 1988), Saanich Inlet (GERMAN and ELDERFIELD, 1989) and the anoxic hypersaline Bannock Basin (SCHIFF *et al.*, 1989a).

DISCUSSION

The current REE data set comprises a suite of vertical profiles of dissolved elements at the BSK-2 site, with additional data for other dissolved and suspended particulate chemical tracers. The major features in these vertical distributions may arise from *in situ* biochemical processes but may also have been produced elsewhere, notably along the margins, and then transported into the center of the basin. The conceptual difference between either *in situ* or advective features has been discussed for the Cariaco Trench (DE BAAR *et al.*, 1988), yet neither in the Cariaco Trench nor in the Black Sea does the modest data set allow us to resolve this issue conclusively.

Fractionation within the REE series is commonly depicted in distribution patterns normalized vs shales, the latter thought to represent crustal abundance, i.e. the average input of REE into the oceans upon continental weathering (Fig. 8). Other normalization standards are conceivable and would represent riverine input after some fractionation within estuaries (GOLDSTEIN and JACOBSEN, 1988; SHOLKOVITZ, 1988). Such alternative normalization would not alter trends within our data set.

Enrichment with atomic number

Generally the shale normalized REE patterns show the gradual enrichment of heavy REE (HREE) typical for seawater. This trend is ascribed to stabilization in solution of

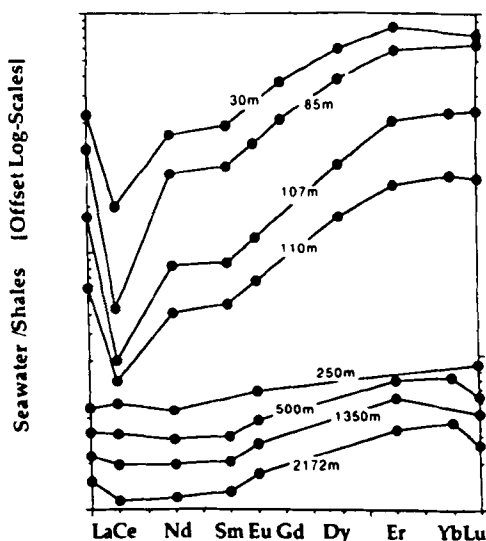


Fig. 8. Patterns of REE in the Black Sea normalized vs crustal abundance (shales). Offset vertical log-scale as to avoid overlapping patterns.

heavier REE by stronger complexation, mostly as carbonate species (BYRNE *et al.*, 1988). Minor deviations from this overall HREE enrichment are discussed below (see also Eu). Otherwise this enrichment of HREE vs light REE (LREE) is most obvious from the elemental ratio Er/Nd (Fig. 9). Er is used here rather than Lu, since the crustal abundance of Lu in shales generally appears to have been overestimated. Seawater Lu/Nd ratios should therefore not be compared to the shale Lu/Nd ratio. Moreover, the overestimation of Lu crustal abundance in shales would account for the fact that in seawater Lu does not always seem to follow the trend of HREE enrichment in the shale normalized patterns (Fig. 8). Otherwise the strong maximum of Er/Nd at 107 m depth coincides with the dissolved minima (Fig. 6) and the onset of the particle maximum (Fig. 7). Presumably the Mn oxides associated with these particles scavenge the LREE (e.g. Nd) more effectively than the HREE (e.g. Er); the latter are after all more stable in solution.

The generally high ratio of Er/Nd throughout the water column ultimately reflects significant HREE enrichment in the source terms, i.e. both fresh water from the major rivers draining into the Black Sea as well as the slowly renewing deep water of Mediterranean origin ($S \approx 38\text{‰}$). We have not yet studied the REE in the river input; however, the surface sample with low salinity ($S = 17.9\text{‰}$) at this station is distinctly HREE enriched. Mediterranean waters on the other hand also exhibit a strong HREE enrichment (SCHIFF *et al.*, 1989a).

Cerium

Virtually throughout the water column dissolved Ce is depleted relative to its neighboring elements La and Nd (Fig. 8). This depletion is obvious from the elemental ratio Ce/Nd (Fig. 9) but is otherwise best expressed as the Ce anomaly Ce/Ce^* (Fig. 10). This Ce anomaly is defined as

$$Ce/Ce^* = [3Ce_{sw}/Ce_{sh}]/[2La_{sw}/La_{sh} + (Nd_{sw}/Nd_{sh})], \quad (2)$$

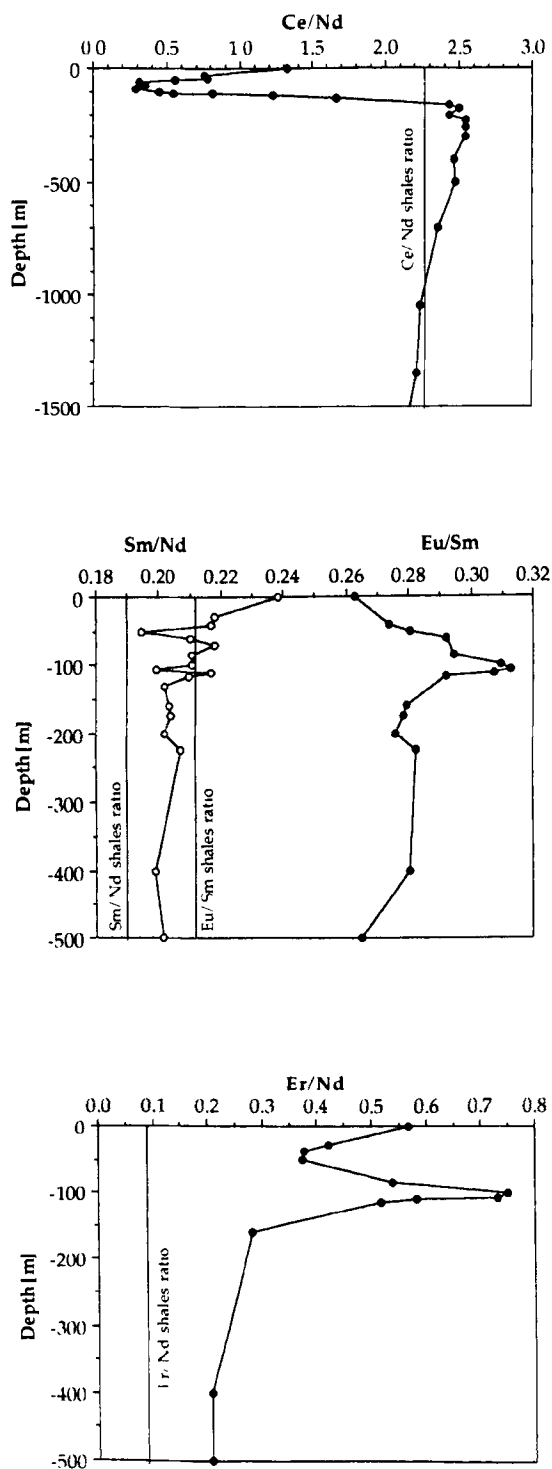


Fig. 9. Vertical profiles of the elemental ratios Ce/Nd, Sm/Nd, Eu/Sm and Er/Nd in the upper 500 m of the Black Sea.

where the subscripts sw and sh indicate seawater concentration and crustal abundance in shales, respectively. The strongest Ce depletion is found within the suboxic zone (85 m). From 160 m to about 600 m depth the Ce anomaly is slightly above the 1.0 value for crustal abundance (shales) with the maximum Ce anomaly of 1.15 at 200 m depth (Fig. 10). The surface sample ($S = 17.9\text{‰}$) at this station has only a modest Ce depletion which might be caused by *in situ* dissolution of some aeolian input. Generally Ce is more strongly depleted than in the Cariaco Trench (DE BAAR *et al.*, 1988). This may reflect a significant Ce depletion in the source terms, i.e. both the slowly renewing deep water of Mediterranean origin as well as fresh water from major rivers draining into the Black Sea which could develop a negative Ce anomaly during estuarine mixing. We have not yet studied REE in the river input but Mediterranean waters exhibit a distinct Ce depletion (SCHIFF *et al.*, 1989a).

The generally high concentrations of Ce and other REE in the anoxic Black Sea are consistent with the more stagnant anoxic deep waters. The longer time for deep water renewal allows the buildup of higher concentrations (SPENCER and BREWER, 1971). However, the measured Ce concentration in the anoxic deep water is still grossly undersaturated relative to the thermodynamic prediction of millimolar Ce levels in sulfidic waters. Within the oxygenated ($\text{O}_2 > 10 \mu\text{M}$) surface waters (0–80 m) dissolved Ce is

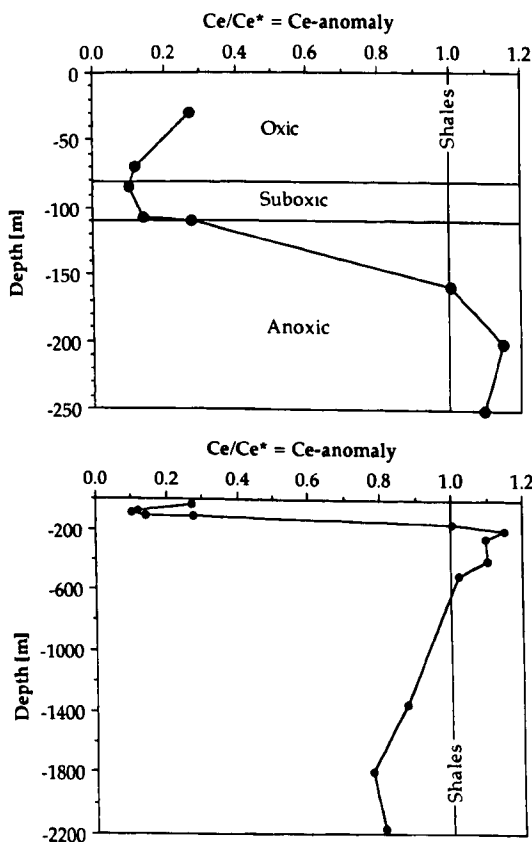


Fig. 10. The dissolved Ce anomaly in the upper 250 m and the complete water column of the Black Sea. $\text{Ce/Ce}^* = (3 \text{ Ce/Ce}_{\text{shales}})/(2 \text{ La/La}_{\text{shales}} + \text{Nd/Nd}_{\text{shales}})$.

oversaturated. For example, at a hypothetically low 1 nM O_2 the dissolved Ce would still be oversaturated; at equally undetectable 1 nM H_2S the Ce would be undersaturated as has been derived from thermodynamic model calculations (DE BAAR *et al.*, 1988). The transition from oversaturation (i.e. dissolved Ce(III) being oxidized) to undersaturation (i.e. particulate Ce(IV) O_2 being reduced) is situated at the suboxic–anoxic boundary. This boundary constitutes a sharp transition for the Ce redox reaction (equation 1).

The vertical resolution of redox environments (i.e. p_e or E_h) now existing in the Black Sea leads to deconvolution of the gradients of dissolved Ce (Figs 5 and 6) and dissolved Mn (Fig. 4). The steepest gradient of Mn is across the oxic–suboxic interface, well above the gradient of Ce which is found at or just below the anoxic interface. The primary particulate Mn maximum is at the same 70–80 m depth range. The nitrite maxima are typically situated within the suboxic zone proper, with varying intensity and depth ranges (Fig. 3). The secondary particle maximum, presumably consisting of bacteria as well as oxidized forms of Fe and Mn and some phosphate, is within the anoxic zone, below the nitrite maxima but just above the steep Ce gradient.

Summarizing, one encounters with increasing density (i.e. depth) in the Black Sea the first small nitrite (NO_2^-) maximum (at $\sigma_\theta = 14.35$ at ~40 m); the nitrate (NO_3^-) maximum ($\sigma_\theta = 15.00$ at ~57 m); the dissolved Mn gradient and particulate Mn maximum ($\sigma_\theta = 15.65$ at ~75 m); the phosphate (PO_4^{3-}) minimum ($\sigma_\theta = 15.72$ at ~80 m); the suboxic interface ($O_2 < 10 \mu M$ at $\sigma_\theta = 15.75$ at ~80 m); the extended Ce minimum ($15.75 < \sigma_\theta < 16.10$ or $80 < m < 107$); the NO_3^-/NH_4^+ transition with second small nitrite (NO_2^-) peak ($\sigma_\theta = 15.9$ at ~93 m); the PO_4^{3-} maximum ($\sigma_\theta = 16.0$ at ~98 m); and the anoxic interface ($H_2S > 1 \mu M$) with minima for all REE, particle maximum, bacterial Chl *a* maximum and secondary Mn particles maximum all at $\sigma_\theta = 16.1$ at ~107 m. Well within the anoxic waters the dissolved Mn, gradients of Ce/Ce* (Fig. 10), Ce proper and the other REE (Fig. 5) culminate in the corresponding dissolved maxima of Mn (~180 m), Ce/Ce* and Ce (at $\sigma_\theta = 16.83$ at 300 m) and the other REE (at $\sigma_\theta = 16.94$ at 400 m).

At the suboxic–anoxic interface the observed Ce concentrations around 4 pM would yield an apparent equilibrium p_e in the 3–4 range (DE BAAR *et al.*, 1988). This brings the onset of Ce reduction just below the redox couple of Mn (p_e about 5, TURNER *et al.*, 1981), below that for nitrate reduction (MURRAY *et al.*, 1983) and above that of Fe reduction (p_e about 1, TURNER *et al.*, 1981). The strong gradient of Ce (indicating reductive dissolution) is indeed well below the Mn gradients and also well below the nitrite peaks indicative of nitrate reduction.

In fact the strongest dissolved Mn gradient is well above the Ce gradient. The dissolved Mn still being fairly high across and above the oxic–suboxic interface suggests the oxidation of dissolved Mn to be rather slow as compared to its upward (apparent) diffusion.

Cycling of all REE

Ce being driven by its own redox chemistry it is remarkable that the other REE also exhibit minima (i.e. scavenging removal) and maxima (i.e. *in situ* dissolution) at exactly the same 107 and 400 m depths, respectively. For the strictly trivalent REE the gradients are more modest (as demonstrated by the Ce/Nd ratio, Fig. 8). Yet it appears as if all REE are either carried along within the Ce redox cycle, or somehow involved with settling (bacterial) particles. Here we note that the 107 m particulate maximum coincides with a

modest yet distinct secondary maximum of particulate Mn (Fig. 3). This coincidence is striking also in the light of experimental evidence for bacterial mediation of Mn oxidation (TEBO, 1991). Given the sheer abundance of nanomolar Mn (possibly as a coating on the bacteria) the latter would be a likely carrier for picomolar amounts of REE to be scavenged and subsequently released. For Ce we envision a reaction sequence where the dissolved Ce(III) is first adsorbed and subsequently oxidized to the Ce(IV) state. This subsequent oxidation of Ce(III) to Ce(IV) would make the overall removal more efficient for Ce (KOEPPENKASTROP and DE CARLO, 1988, 1990). Upon settling the reductive dissolution of Mn oxides and Ce oxides would release all REE from the particles, the effect being most pronounced for Ce, yielding the observed strongest gradients for Ce relative to the other REE.

The very shape of the dissolved profiles (Fig. 5) is most tempting for application of a simple vertical model combining vertical transport (settling and apparent diffusion) with chemical kinetics of *in situ* oxidation and *in situ* dissolution (SPENCER and BREWER, 1971). Upon future analyses of the suspended particles we will entertain such an exercise.

From the distribution of naturally occurring Ce and other REE it is obvious that the downward transport of Chernobyl radionuclides ^{144}Ce and ^{147}Pm with settling particles will be somewhat counteracted by dissolution within the anoxic waters. The downward particulate flux of ^{144}Ce as collected in sediment traps was indeed reported to be less in the deeper trap (BUESSELER *et al.*, 1989). Substantial radioactivity of ^{144}Ce was found at the seafloor underlying our Sta. BSK-2 (O'NEILL and MOORE, 1990).

Europium

At first glance Eu does not behave differently from other LREE such as Nd or Sm (Figs 5 and 6). Apparently the reduction of Eu(III) to Eu(II) does not take place. Detailed plots of the elemental ratio Eu/Sm exhibit a distinct Eu enrichment at 107 m depth (Fig. 9), whereas at best a weak Eu/Sm maximum was observed in the Cariaco Trench. Due to its higher atomic number Eu is expected to be more strongly complexed, i.e. more stable in solution than Sm (BYRNE *et al.*, 1988). Scavenging by Mn oxide coatings would affect the lighter REE (Nd, Sm) more strongly. In this respect the Eu/Sm maximum at 107 m in the Black Sea is analogous to the Er/Nd maximum (Fig. 9); the latter is expressed more strongly due to the greater difference in atomic number (Er–Nd = 8 vs Eu–Sm = 1). Within this context the ratio Sm/Nd (reflecting two atomic number units difference) would also be expected to show a distinct peak at 107 m depth. In fact there is no such feature in the Sm/Nd profile (Fig. 9). From the REE patterns in the Black Sea (Fig. 8) and elsewhere (DE BAAR *et al.*, 1988; GERMAN and ELDERFIELD, 1989) it is obvious that the true enrichment of the HREE only begins at the Sm–Eu interval. In fact both Nd and Sm are often found to be significantly depleted relatively to both La and Eu (Fig. 8). Such depression of the Nd–Sm couple is a challenge for the currently available solution models (BYRNE *et al.*, 1988). These models are partly based on interpolation within the REE series and predict the general REE enrichment with increasing atomic number to be rather monotonous. The observed excursions from this trend in seawater might require more elaborate assessment of individual stability constants of, e.g. La, Nd, Sm, Yb and Lu (DE BAAR *et al.*, 1991).

Nonetheless, reduced Eu(II) would likely be more strongly complexed (stable) in solution, i.e. would also move the Eu/Sm ratio in the upward direction. This might contribute to the observed Eu/Sm peak but can otherwise not be resolved with any

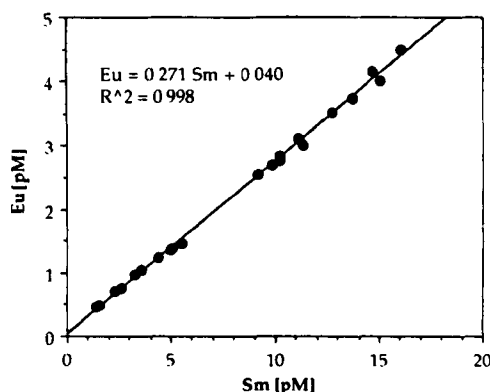


Fig. 11. Linear regression of dissolved Eu vs dissolved Sm in the Black Sea.

significance. At greater depth no scavenging Mn oxides phases exist and any Eu(II), if existing at all, would not become fractionated from Eu(III) or Sm(III). In fact a linear regression (Fig. 11) of the complete data set

$$\text{Black Sea: } \text{Eu} = 0.271 \text{ Sm} + 0.0405 \quad r^2 = 0.998 \quad (3)$$

is virtually identical to earlier results

$$\text{Cariaco Trench: } \text{Eu} = 0.262 \text{ Sm} + 0.007 \quad r^2 = 0.969 \quad (4)$$

$$\text{Bannock Basin: } \text{Eu} = 0.26 \text{ Sm} + 0.12 \quad r^2 = 0.99 \quad (5)$$

These anoxic basins do not deviate from typical open ocean ratios of about $0.22 < \text{Eu}/\text{Sm} < 0.26$ (DE BAAR *et al.*, 1985a). Finally, thermodynamic considerations would not favor Eu(II) under low temperature reducing conditions either (SVERJENSKY, 1984).

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